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Ennoblement: Due to Big Films: Indicator for Potential Corrosion & Source of Electrical Energy

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Ennoblement Due to Biofilms: Indicator for Potential Corrosion and Source of Electrical Energy

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Abstract: Ennoblement, a positive shift in corrosion potential, due to biofilm formation is the basis of patents for biofilm monitoring and power generating devices. Ennoblement is a global phenomenon that is routinely cited as a mechanism for microbiologically influenced corrosion of some passive alloys. Increased corrosion is attributed to acceleration of the oxygen reduction reaction via several potential mechanisms that have been debated for decades. Because the phenomenon is predictable and reproducible at specific locations, ennoblement is the basis for patented methods and devices for monitoring biofilm formation and relating ennobled potentials to increased likelihood of corrosion and for evaluating cleaning and biocide treatments. Furthermore, when anodes and cathodes can be separated, as in a microbial fuel cell, biofilm formation on the cathode increases the potential difference between the two and the resulting power output. Most patented fuel cells using metal cathodes do not refer specifically to ennoblement in the disclosures.

Keywords: Biofilms, ennoblement, microbial fuel cell, microbiologically induced corrosion, microbiologically influenced corrosion, oxygen reduction reaction, redox-active compounds, seawater battery.

1. INTRODUCTION

Biofilms cause a noble shift, or ennoblement, in corrosion potential (E_{corr}) for most passive alloys and noble materials. Ennoblement is a global phenomenon which has been studied intensely since the 1980's as a mechanism for microbiologically influenced corrosion (MIC). Theoretically, E_{corr} ennoblement should increase the probability for pitting and crevice corrosion initiation and propagation for those passive alloys where E_{corr} is within a few hundred millivolts of the pitting potential (E_{pit}). The metals and alloys tested include but are not limited to: stainless steels [1-7], nickel [8, 9] and nickel-based alloys [6, 10], titanium [5, 6, 8, 9, 11, 12], copper-nickel [5, 9, 11, 13], and noble metals [5, 8] (Fig. 1). Ennoblement has also been reported for graphite and glassy carbon electrodes in marine and freshwater environments [14, 15].

Little *et al.* [16] reviewed mechanistic interpretations of ennoblement in marine waters, but a unifying explanation for all observations does not exist. Numerous researchers have shown that increased cathodic reduction rates accompany ennoblement of E_{corr} [5, 7, 11, 13]. Little and Mansfeld [17] categorized the proposed mechanisms for ennoblement in marine environments into three categories: thermodynamic, kinetic, and alteration of the nature of the reduction reaction. Thermodynamic arguments for ennoblement suggest that either a pH decrease at the metal/biofilm interface or a

local increase of the partial pressure of oxygen (p_{O_2}) raises the reversible potential of the oxygen electrode ($E_{\text{O}_2}^0$). For aerobic biofilms, changes in $E_{\text{O}_2}^0$ due to changes in p_{O_2} would be small. However, a decrease of local pH from 8 to 3 would account for an ennoblement of about 300mV, assuming that the exchange current density for the oxygen reduction reaction (ORR) ($i_{\text{O}_2}^0$) and the cathodic Tafel slope remain constant (Fig. 2) where the initial E_{corr}^1 changes to E_{corr}^2 as $E_{\text{O}_2}^{0.1}$ increases to $E_{\text{O}_2}^{0.2}$.

Little *et al.* [18] measured E_{pit} in abiotic chloride solutions at pH = 4 and 2 and observed that E_{pit} decreased below E_{corr} values determined in natural seawater, and therefore dismissed the possibility that ennoblement was due to reduction of surface pH. This conclusion was challenged by Chandrasekaran and Dexter [19] who suggested that E_{pit} for a stainless steel covered by a biofilm might be different from that measured in an abiotic solution. Nevertheless, the same authors conceded that "all the observed ennoblement on stainless steel, particularly in low salinity waters, cannot be explained by pH alone." Mollica *et al.* [4] analyzing field test data, concluded, "the phenomenon of oxygen depolarization on active-passive alloys covered by slime does not depend on acidification of the substrate but, on the contrary, on a light (sic) alkalization."

Kinetic arguments for ennoblement suggest that the rate of ORR at a given potential can also increase due to an

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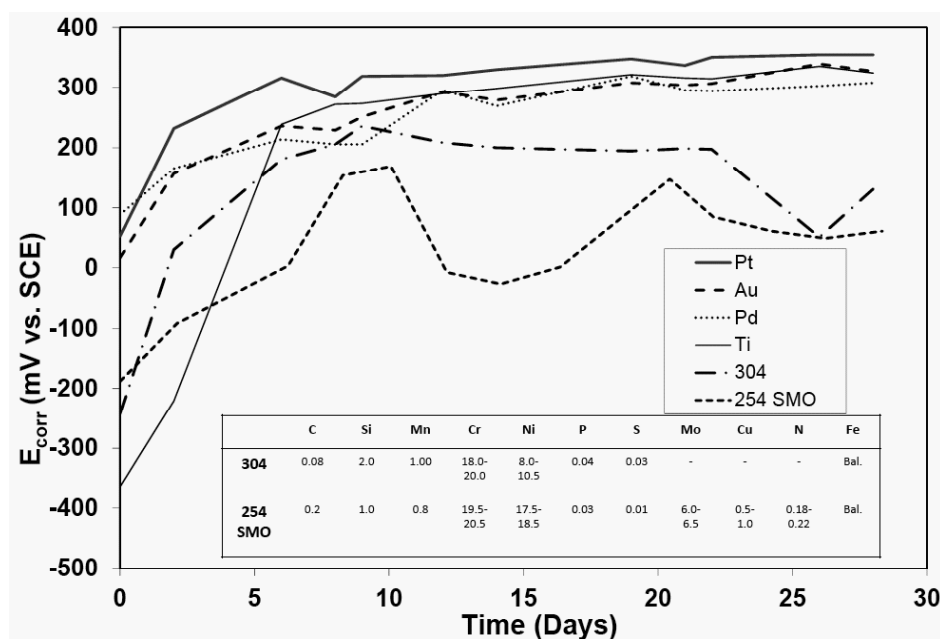


Fig. (1). Composite of E_{corr} vs. time data for materials exposed in natural seawater.

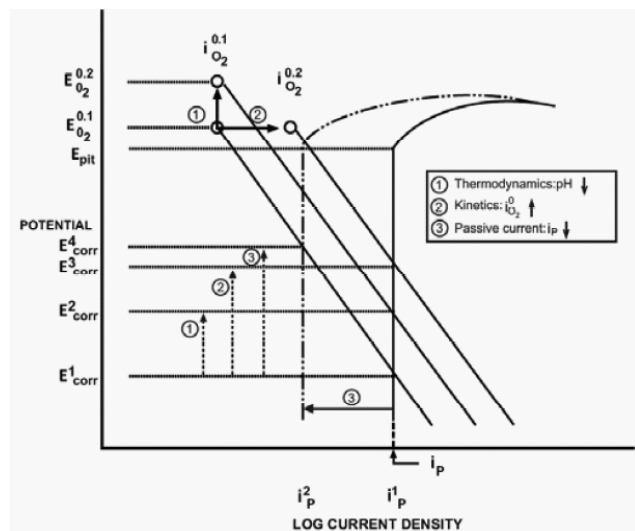


Fig. (2). Schematic polarization curves for stainless steel in seawater.

increase of $i_{\text{O}_2}^0$ (from $i_{\text{O}_2}^{0.1}$ to $i_{\text{O}_2}^{0.2}$) leading to an increase of E_{corr}^1 to E_{corr}^3 (Fig. 2). Dexter and Gao [20] suggested that increased oxygen reduction rates could be due to an increase of $i_{\text{O}_2}^0$, mediated by biopolymer metal complexes known to catalyze the ORR. The nature of these organometallic catalysts has been the topic of wide discussion [11]. Holthe *et al.* [5] referred to biofilm catalysis of oxygen reduction. Scotto *et al.* [3] attributed catalysis to the presence of microbial enzymes and based this assertion on the abrupt drop in ennobled E_{corr} that accompanied addition of a respiratory inhibitor, sodium azide, to a microbial film.

Srinivasan *et al.* [21] pointed out that enzymes could accelerate electrochemical reactions and noted the inhibitory effect of sodium azide on enzyme electrocatalysis of oxygen reduction. They further reported that lactase increased $i_{\text{O}_2}^0$ on platinum approximately 40 times above that observed in the absence of the enzyme. Johnsen and Bardal [2] observed that the presence of a biofilm dramatically increased the current density required to polarize stainless steel to a potential of -400mV (vs. saturated calomel electrode (SCE)), adequate to provide cathodic protection in seawater. They attributed this increase to a lack of calcareous deposits and an enhanced oxygen reduction rate beneath the biofilm due to an increase of $i_{\text{O}_2}^0$. The mechanism of organometallic catalysis has been criticized, however, because ennoblement is also observed on more noble metals, including titanium and platinum, which lack transition elements thought to be necessary to form catalyzing complexes [22].

Theoretically it is also possible that E_{corr} becomes ennobled due to a decrease of passive current density (i_p) from i_p^1 to i_p^2 at constant $E_{\text{O}_2}^0$, $i_{\text{O}_2}^0$, and Tafel slope, leading to a change from E_{corr}^1 to E_{corr}^4 (Fig. 2). Eashwar and Maruthamuthu [23] proposed a mechanism in which siderophores (iron chelators) produced by microorganisms within biofilms at neutral pH act as inhibitors and enhance passivity of the stainless steel by reducing i_p . Hansen and McCafferty [24] demonstrated that a bacterial siderophore, parabactin, had an inhibiting effect on E_{pit} for aluminum in NaCl. Eashwar *et al.* [25] predicted that siderophore production and maximum ennoblement occur at pH 8. Their proposed model has not been rigorously tested, but it does explain the observations by Scotto *et al.* [3] of a drop in E_{corr} with the addition of so-

dium azide. The respiration inhibitor would prevent formation of siderophores. The theory is also consistent with the observation that very noble E_{corr} values are often maintained for long periods of time without any indication of localized corrosion. Eashwar has called the theory "imaginary, but ... based on careful analysis of both the literature on ennoblement and ecological factors inherent in marine biofilms."

In the previous discussion, it was assumed that microorganisms change the rate of the cathodic reaction and for neutral, aerated solutions, the cathodic reaction is ORR. It is possible that microorganisms change the rate-determining step in an electrochemical reaction or produce an entirely different mechanism. Chandrasekaran and Dexter [19] suggested that reduction in surface pH and production of hydrogen peroxide (H_2O_2) at low oxygen concentration were important contributory factors for ennoblement. The contribution of H_2O_2 to ennoblement is associated with its relatively noble thermodynamic potential at low pH. Theoretically, at pH = 2.9 and $p_{\text{O}_2} = 0.5\text{ppm}$, the presence of 8.2mM H_2O_2 would produce an increase in the reversible potential of 0.5V. These specific conditions have not been measured in an actual biofilm. Chandrasekaran and Dexter [19] measured H_2O_2 concentrations ranging from 1.3 to 6.6mM on biofilm coated platinum coupons after a 1-year exposure. Dupont *et al.* [26] observed ennoblement of stainless steels exposed in "biochemical artificial seawater," a chemically defined seawater amended with glucose and glucose oxidase. The enzyme catalyzes the oxidation of glucose to gluconic acid and H_2O_2 . Dickinson and Lewandowski [27] listed redox active constituents that could be produced within biofilms and that could be a part of the electron transport system, including, the oxidized form of nicotinamide adenine dinucleotide, flavin-adenine dinucleotide, quinones and metallo-porphyrins.

Ennoblement in fresh and estuarine waters is related to microbial manganese oxidation and deposition coupled to bacterial cell growth and metabolism of heterotrophic substrates [28-30]. The reduced form of manganese, Mn^{2+} is soluble, while the oxidized forms, Mn_2O_3 , MnOOH , Mn_3O_4 , MnO_2 , are insoluble. Manganese oxides can be deposited on submerged materials including metal, stone, glass, and plastic and can occur in natural waters with manganese levels as low as 10-20ppb [31]. Deposition rates of 1 mCoul $\text{cm}^{-2}\text{day}^{-1}$ on stainless steel have been observed [32].

Manganic oxides, including those resulting from microbial activity, i.e., biomineralization, are efficient cathodes. Microbially deposited manganese oxide on a stainless steel in fresh water caused an increase in E_{corr} and increased cathodic current density at potentials above -200mV (vs. SCE) [32]. Passive metal corrosion currents of the order 10nA cm^{-2} allowed biomineralized material to accumulate. E_{corr} then shifted in the noble direction with increasing areal coverage anodically polarizing the metal. E_{corr} may exceed the pitting potential for low molybdenum stainless steels in dilute chloride media, increasing the risk of pit nucleation. Once nucleation occurred, cathodic current sustained by the MnO_2 cathode impeded repassivation by holding the corrosion potential above the protection potential. More available cathode material supported a greater number of pitting sites, increas-

ing the probability that a metastable site became fixed. Localized corrosion current that exceeded the biomineralization rate discharged the oxide cathode so that eventually the corrosion rate was limited by the oxide biomineralization rate and by availability of other cathodic reactants (typically dissolved oxygen). Similarly, *Leptothrix discophora* SP-6, a manganese oxidizing bacterium, modified the surface of a glassy carbon electrode and caused ennoblement [33].

2. ENNOBLEMENT MONITORING

Because ennoblement is a global phenomenon and easily measured with a potentiostat, it is the basis for several patented methods and devices for monitoring MIC (also referred to as microbiologically induced corrosion in some patents). Zero resistance ammeter (ZRA) measurements have been used for many years to monitor the electrochemical impact of microorganisms on metal surfaces in laboratory experiments [34]. Concentric ring electrodes have been used to examine the impact of physical separation of anodes and cathodes on MIC. Polarization was employed to precondition the electrodes for preferential regions of microbiological activity. However, motivation for polarization differed into two distinct categories: 1) mimic corrosion sustained by biofilm formation [35, 36] and 2) monitor biofilm formation through measurement of electrochemical parameters [37].

Angell *et al.* [35] used a concentric ring 304 stainless steel electrode to demonstrate that a consortium of sulfate-reducing bacteria (SRB) and a *Vibrio* sp. maintained a galvanic current between the anode and cathode. In their electrode design, pitting was induced by passage of a 11 $\mu\text{A cm}^{-2}$ current density to a small (0.031 cm^2) anode. The anode was concentric to, and separated from, the cathode (4.87 cm^2) by a polytetrafluoroethylene (PTFE) spacer. Current was applied for seventy-two hours either during or after microbial colonization. Once the applied current was removed the resultant galvanic current flowing between the anode and the cathode was monitored by a ZRA. They found that a current was maintained in the presence of a microbial consortium. No current was measured in a sterile control. The concentric ring electrode provides a technique by which MIC can be studied and is not intended to represent any natural situation.

In similar experiments, Champaignolle and Crolet [36] used a concentric ring carbon steel (CS) electrode to examine stabilization of pitting corrosion by SRB. The same electrode geometry as employed by Angell *et al.* [35] (Fig. 3) was used and a current density of 1.5mA cm^{-2} was applied to the anode for forty-eight hours to induce corrosion in deoxygenated nutrient-enriched synthetic seawater. During this preconditioning period, the test medium was inoculated with *Desulfovibrio vulgaris* while a sterile condition was monitored as a control. In the presence of *D. vulgaris*, a residual galvanic current was obtained while no current was measured in the sterile control. SRB were shown to stabilize pitting corrosion of CS by maintaining a stable galvanic current between a local anode and a surrounding cathode.

One commercially available on-line monitoring technique [38] and device [39] for biofilm development uses a probe made up of a series of identical stainless steel discs (Fig. 4) [40]. One set of these discs is polarized relative to

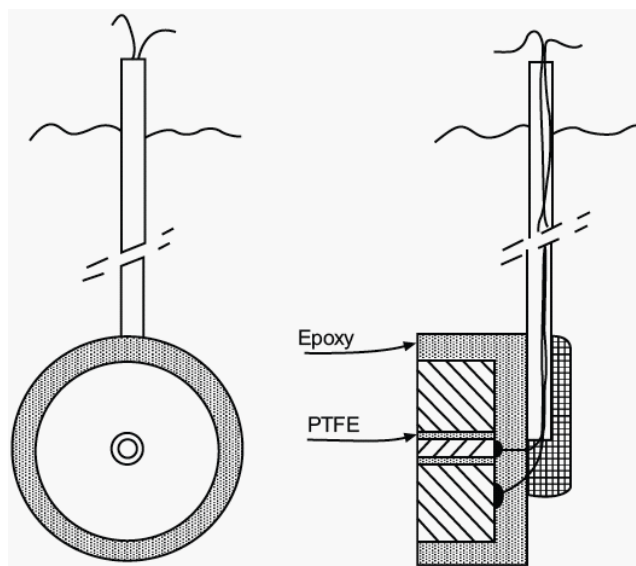


Fig. (3). Schematic of concentric ring electrodes [36]. Reproduced with permission from NACE International.

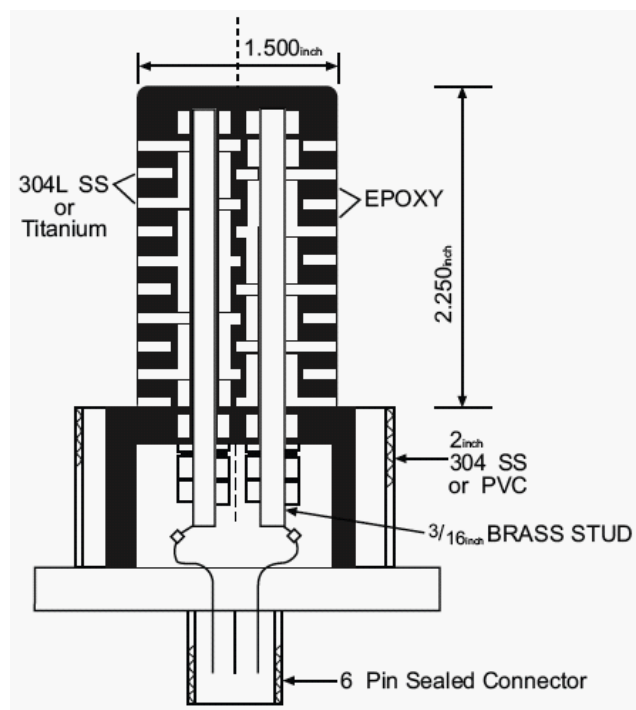


Fig. (4). BIOGEORGE® Probe [40]. Reproduced with permission from NACE International.

the other for approximately 1hr/day, maintaining the same polarity. During the measurement periods, the electrodes are connected through a ZRA and currents and potentials are monitored continuously. Deposits that induce an increase in the current required to achieve the applied potential, such as biofilms, are detected. Removal of biofilms or treatment with biocides results in an immediate decrease in the current. The device has been used in fire protection systems, emergency service water stands and essential equipment cooling water

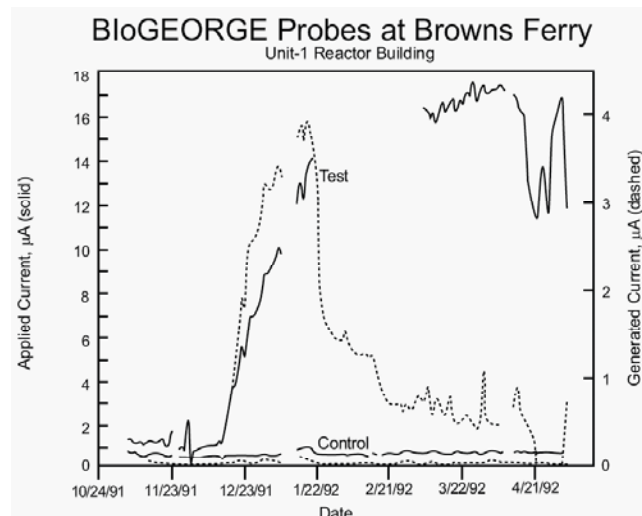


Fig. (5a). Data from Browns Ferry Nuclear Plant – Fire Protection System [40]. Reproduced with permission from NACE International.

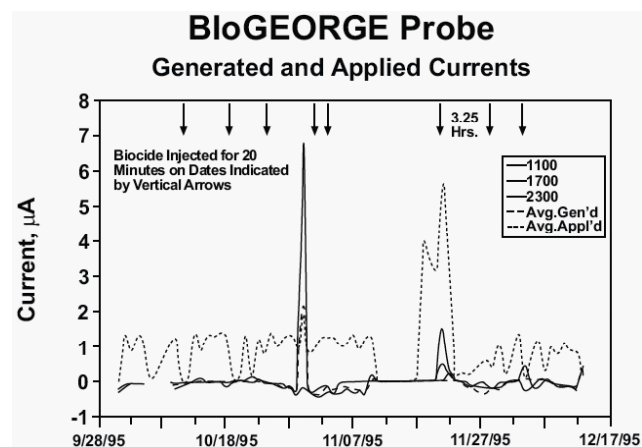


Fig. (5b). Data from Susquehanna – Emergency Service Water Test Stand [40]. Reproduced with permission from NACE International.

systems in nuclear power plants (Fig. 5a-5b) [40]. The device provides a warning when the biofilm maintains a certain current so that the system can be cleaned or biocides can be added. This technique only indicates a corrosion risk. It does not measure any specific property of biofilms or any parameter related to corrosion. According to the inventors, the low level of polarization of the cathode may also encourage microbial colonization. Lee *et al.* [41] demonstrated that polarization did not necessarily encourage biofilm formation in natural water or in artificial media and that under all circumstances the biofilms that formed after a few hours exposure to intermittent polarization did not resemble the biofilms that formed on unpolarized surfaces in the same medium in terms of areal coverage and microbial composition.

Mollica and Ventura [42] used a galvanic couple between a stainless steel pipe and a copper/zinc pipe to monitor biofilm growth on surfaces exposed to natural seawater. Results of the field test showed a measurable increase in the galvanic current due to biofilm and a current decrease after chlorination. They concluded that the device allowed optimization of

antifouling treatments by controlling chlorine concentrations and frequency of injections to minimize biofilm recovery rate. The patented version of the device [43] is commercially available. Similarly, in 2005 Marchal *et al.* [44] patented a “Method and Device for Detecting Microbiologically Induced Corrosion.” The sensor consisted of two concentric rings. By applying a “preconditioning current” the rings are polarized so that the smaller one becomes the anode and the other one becomes the cathode. The purpose of the invention is to initiate and localize corrosion. The inventors assume that bacterial growth occurs more readily on the cathode. After polarization the two electrodes are galvanically coupled and current or potential difference is measured between two electrodes and a corrosion rate is calculated.

3. MICROBE-BASED POWER SOURCES

Since 2005 there have been no further developments for using ennoblement by biofilms as monitoring tool. However, research using the same principles to produce microbe-based power sources (microbial fuel cell [MFC] or bacterial battery) has grown at an exponential rate due to an intensified interest in finding viable alternative energy sources for the future. Both bacterial batteries and MFC contain concepts predicated on the ennoblement of metals by bacterial biofilms. These power sources are galvanic cells consisting of two chambers with at least one containing a microorganism that will catalyze electron transfer to/from an electrode [45–48] (Fig. 6). Despite the similarities of bacterial batteries and fuel cells (and their questionable classifications in the literature), one aspect that differentiates a system as a bacterial battery or MFC is that a battery converts stored chemical energy while a fuel cell converts external fuel sources to energy. Unfortunately, research in this area has not been rigorous in making this distinction as fuel cells have found broader interest than battery concepts to date [46, 49]. For example, the sediment MFC design reported by Shantram *et al.* [50] is by definition a bacterial battery. The published system contained a sacrificial magnesium alloy anode while the cathodic reaction was supported on a stainless steel cathode for the cycling of MnO_2 with a bacterial biofilm.

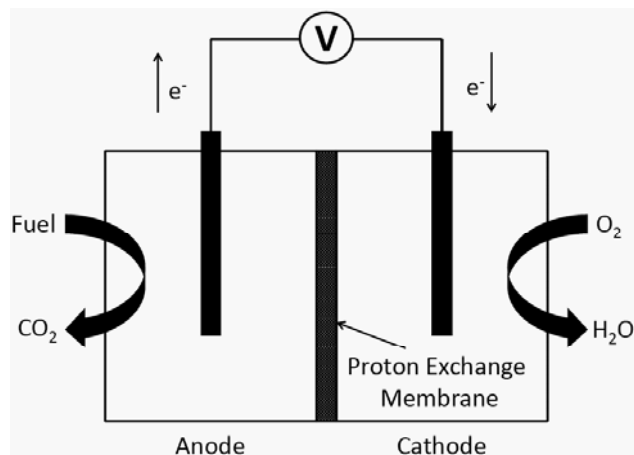


Fig. (6). Schematic and principles of conventional microbial fuel cell.

Bacterial batteries and MFCs share a similar lineage with the original disclosures published in the mid 1960's. The

priority application for bacterial batteries [51] (and by analogy the process of ennoblement to generate a biological power source) pre-dates the submission of the first patent on MFCs by approximately seven years [52]. Overall, the battery patents are primarily focused on biofilms and the corrosion of alloys, copper, manganese, and magnesium with different system architectures and designs. In contrast, the patents for the concept of a “microbial fuel cell” can be separated by either 1) systems and concepts that generate electricity or 2) systems designed to generate fuels using reduction mechanisms at the cathode. Oxygen is the most suitable electron acceptor for these devices due to its high oxidation potential, availability, and low cost.

Some of the earliest examples of exposing metals to corrosion as a method to generate a current were presented with sea water batteries. The first patent (including an international French filing) disclosing the concept of a sea water battery was in 1993 by Hasvold and Garshol but the patent does not address biofouling specifically and basically describes a design where alloys and metals are made into a galvanic cell in sea water [53]. Their patent was later followed by the first publication of their system in 1997 [54]. A general version of this battery configuration was patented in 1977 but did not specifically discuss biofouling mechanisms [55]. An underwater defense system was disclosed that facilitates communication between unmanned underwater vehicles using a salt water battery power source [56].

4. DESIGN OF A MICROBIAL BATTERY

Daumas *et al.* [57] were the first to specifically define a “microbiological battery” using a salt bridge electrochemical design and only bacteria to generate each half cell reactions. This experiment correlated ennoblement as a potential design feature for bacteria batteries and ultimately MFCs using only microorganisms. Additionally, the biofilm-covered stainless steel cathode supplied a current density up to 140 mA/m^2 at $+0.05 \text{ V vs. Ag/AgCl}$ and it was concluded that biofilm-covered stainless steel cathodes were promising candidates for catalyzing the ORR for power production.

5. DESIGN OF A MICROBIAL FUEL CELL (MFC)

A conventional MFC consists of an anaerobic biological anode and abiotic aerobic cathode where electrons are transferred to oxygen as the terminal electron acceptor [48, 58]. Basic designs include an anaerobic anode chamber that contains bacteria and possibly electron shuttles/mediators as well as a conductive anode. The oxygen-rich cathode chamber typically contains a conductive cathode and biocatalysts that promote oxidation reactions. The two chambers are separated by a proton exchange membrane (PEM).

5.1. Methods to Improve Power Output

5.1.1. Modify the Proton Exchange Membrane (PEM)

Original MFC components included artifacts from the standard H_2/O_2 PEM fuel cells including using Nafion™-117 cation exchange membranes even though they are not designed for ambient temperature used in MFCs or neutral pH. One of the original patents addressing using alternative neutral nanoporous membranes in biological fuel cells was just

recently accepted [59] and other modified PEM patents using porous frit composite PEM have also recently been published [60]. The pores of the porous frit are filled with a proton-conducting material. The idea of modular and interchangeable units including membrane assemblies in form of cassettes has also been protected and covers future engineering considerations like cell failure and maintenance of constant power output for biological fuel cells [61].

5.1.2. Modify the Electrolytes

Electrode efficiency and increased power output can be accomplished by modifying electrolytes or by introducing flow. Cardenas-Valencia *et al.* [62] added a halogen salt oxidizer in the cathode chamber to increase power output. Newman *et al.* [63] patented “Redox-Active Compounds and Related Compounds, Methods and Systems” to affect production and/or activity of microbiologically produced redox active compounds for use in the anode chamber of MFC. Several authors have demonstrated that microbiologically produced flavins, pyocyanin and phenazine enhance electron transfer in MFC [64-66]. Keller *et al.* [67] designed a continuous loop system where the effluent generated in the anode flowed into the cathode and vice versa.

5.1.3. Modify Electrodes (Biotic and Abiotic Coatings)

Typical MFC designs use unmodified carbon based materials as electrodes for phototrophic [68] and non-phototrophic research [69, 70]. The graphite electrodes that are commonly used in these designs are not able to fully exploit oxygen as an electron acceptor because of large potential losses. Since, the operational pH of biological power sources is between 6-8, many of the conventional precious and transition metal catalysts are not applicable for MFCs because of rapid deactivation, slow kinetics at neutral pH, and incomplete reduction of oxygen to reactive oxygen species and radicals [71, 72].

Modifications of electrode surfaces have been used to increase cell efficiency. Designs may include electrically conducting polymers coated on the anode or metal coated cathodes to facilitate electron shuttling. Ringeisen and Biffinger [59] discuss a metal coated cathode by coating with a solution of 60% water, 35% isopropanol, 5% of a 5% nafion solution and 10 mg of a 20% platinum particles with vulcanized rubber.

There are several patents and patent applications focused on the utilization of biofilm-coated alloy electrode (and resulting ennoblement) to generate a current from biological power sources. This collection of patents can be separated into systems that are designed for direct application of biofouled metal electrodes in water for power output [73-75] or generation of hydrogen using biofilm coated alloy cathodes [76-78]. The physical properties of these cathode surfaces for microbial attachment have also been published recently [79, 80]. He and Angenent [47] recognized that biocathodes could be beneficial for MFC and discussed both aerobic biocathodes (oxygen as the terminal electron acceptor) and anaerobic biocathodes (something other than oxygen as electron acceptor, e.g., nitrate, sulfate, iron, manganese, selenate).

As previously discussed, biofilms can lead to a cathodic shift in metal redox potential and thus could be used to increase the efficiency of unmodified alloys for the ORR. One of the first examples of a laboratory fuel cell exhibiting an enhancement of the cathode by biofouling was published by Bergel *et al.* in 2005 [81]. The experiment was based on using a classic H_2/O_2 PEM fuel cell design exposed to sea water from Genova Harbor (Italy). The anode was platinum and the cathode was stainless steel. Their data indicated that a biofilm was formed on the stainless steel cathode and demonstrated that ennoblement could generate a current density of $1.89 A/m^2$. The mechanism for this enhancement is a topic of great interest considering the number of potential variables (reactive oxygen species, oxide layer activity, bacterial interaction with surface, secretion of redox active proteins and metabolites) [82]. The use of ennoblement to generate a power source was tested by Kus *et al.* [83]. They demonstrated that one type of bacteria could shift E_{corr} of one metal in the positive direction (ennoblement) while another organism could shift E_{corr} of another metal in the negative direction to produce a larger cell voltage than the same battery that did not contain bacteria [83, 84]. Nguyen *et al.* [33] suggested that bacterially deposited manganese oxides on carbon electrodes could be used as cathodic reactants, “significantly superior to oxygen,” producing a current density up to two orders of magnitude higher than those reached with reduction of oxygen.

Enhancement of electrode architecture has led to new and amendable materials to improving the contact between microorganisms and the electrode surface ultimately to include alloys and metals. Several groups have published methods to improve bacterial attachment to the anode using electrically conducting nanofibers where a portion of the electrically conducting fibers is in contact with the anode or cathode [85]. Salguero *et al.* [86] designed an ordered 3-D electrode surface to allow for better nutrient diffusion through the electrode. Enhanced power output is attributed to increased biofilm thickness and viability of microorganisms within the 3-D structure.

Alfonta *et al.* [87] protected a method for using genetically modified prokaryotic and eukaryotic cells for expressing applicable proteins to the outer membrane surface to improve fuel oxidation or extracellular electron transfer in biological fuel cells for alcohol oxidation or oxygen reduction. According to the patent application, red/ox enzymes or hydrolases are localized on the surfaces of cells to optimize site-specific immobilization

In addition to power applications, microbial cathodes are being evaluated for the reduction of CO_2 to methane and other short chain carboxylic acids [88, 89]. However, the researchers involved in publication of the reduction of CO_2 are not involved in any of the pending patent applications that include biofilms and alloy based materials [90, 91].

5.2. Growth of Unwanted Microorganisms

Growth of unwanted microorganisms in the cathode chamber and in the PEM is impossible to avoid. Microbial fouling reduces the efficiency of cation transfer across the membrane. One alternative to the use of a PEM uses glass

wool or glass beads as a barrier between cathode and anode [92]. Both are subject to unwanted colonization by bacteria.

It is also possible to eliminate the need for a membrane by using seafloor devices or benthic MFC (BMFC) that eliminate the need for the PEM by placing the anode in sediment and the cathode in open water. A BMFC generates power by oxidizing organic matter residing in the sediment pore water with oxygen in the overlying water. It typically includes a non-corrosive anode (graphite) embedded in marine sediment and connected by an external circuit to a non-corrosive cathode (graphite) in the overlying water. The BMFC uses biofilms that spontaneously form on the electrode surfaces to catalyze anodic and cathodic reactions [93]. The potential difference creates a near perpetual generation of current. Xu *et al.* [94] demonstrated ennoblement of E_{corr} on graphite as a result of marine biofilm formation, similar to that reported for metals. Traditional BMFC were large and fragile. Tender [95] patented a bottlebrush electrode residing within a permeable tube that could be used as anode or cathode in a BMFC. A bottlebrush electrode refers to an electrode having a plurality of electrochemically active conductive fibers uniformly distributed and extending outward from the main axis of a current collecting conductive body. Graphite bottlebrush electrodes are especially effective at using oxygen in moving seawater.

Cathodes are current-limiting in some MFC designs [71]. Microbial biofilms on the cathode can have a deleterious effect on the ORR by covering active metal sites with polysaccharide biofilms creating an electrode that could not be enhanced through the process of ennoblement. This fact has resulted in a patent that uses silver, platinum, nickel, copper, or zinc nanoparticle catalysts as antimicrobial coatings to impeded biofilm formation and create more robust cathode electrodes for wastewater applications [96].

6. CURRENT & FUTURE DEVELOPMENTS

Devices that measure ennoblement as a function of time are used successfully in many industrial applications to plan cleaning cycles and biocide concentrations and addition intervals. However, because there is no universally accepted mechanism for acceleration of ORR by biofilms and the devices do not measure a specific property of the biofilm, operators must understand their individual plants/systems before interpreting ennoblement data. Only bacterial batteries and MFC involving alloys and metals can fully benefit from biofilm induced ennoblement and biologically accelerated ORR. The majority of recent MFC patents and applications describe systems that use carbon (graphite) based cathode architectures as support for ORR catalysts or ammonia oxidation under aerobic conditions. Biofilm formation in these systems is a nuisance and can decrease the lifetimes of these devices by inhibiting oxygen availability to the cathode. The logical extension of these systems for long duration deployment would be ennoblement enhanced cathodic materials using metals.

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CONFLICT OF INTEREST

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